

Mechanisms of Concrete Damage Caused by Sulfate Attack Examined through Transmission X-ray Microscopy

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INTRODUCTION

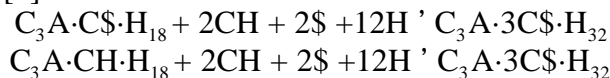
Increasingly often, concrete is the material of choice for the construction of structures exposed to extreme conditions whether it be offshore oil platforms in icy water or hazardous waste containment vessels buried in the earth. As demand for construction in harsh environments increases, so do the desired service lives of these structures. Typically, concrete structures are designed to perform, with minimal maintenance, 50 to 100 years. Concrete containment vessels, which may be hold chemical and radioactive waste, are designed for 500 year service lives and a desire exists to extend the expected service life to 1000 years.

Sulfates present in soils, groundwater, sea water, decaying organic matter, and industrial effluent surrounding a concrete structure pose a major threat to the long term durability of the concrete exposed to these environments. Sulfate attack of concrete may lead to cracking, spalling, increased permeability, and strength loss. Thus, resistance of concrete to sulfate attack is integral to ensure satisfactory performance over long periods.

While the objective is the avoidance of sulfate-related durability problems, this goal is difficult to achieve oftentimes because the mechanisms of expansion caused by sulfate attack in concrete are not well understood. The aim of an ongoing research investigation at XM-1, a transmission x-ray microscope owned and operated by the Center for X-ray Optics (CXRO) at beamline 6.1, is to gain knowledge about the means by which sulfate attack damages concrete.

ETTRINGITE FORMED BY SULFATE ATTACK OF CONCRETE

Sulfates present in soils, groundwater, sea water, decaying organic matter, and industrial effluent surrounding a concrete structure may permeate the concrete and react with existing hydration products. In the presence of calcium hydroxide (CH) and water (H), monosulfate hydrate ($C_3A \cdot C\$ \cdot H_{18}$) and calcium aluminate hydrate ($C_3A \cdot C\$ \cdot H_{18}$) react with the sulfate (\$) to produce ettringite ($C_3A \cdot 3C\$ \cdot H_{32}$) [1]:



In hardened concrete, the formation of ettringite by sulfate attack *can*, but does not always, result in expansion and lead to cracking of the concrete. The conditions under which ettringite formation produces damage in the concrete are uncertain.

It should be noted that ettringite produced by the reactions described above occupies a smaller volume than the reactants occupied. Therefore, the reaction described above must not be responsible for the expansion. It is generally accepted that the expansion caused by sulfate attack is the result of a particular mechanisms associated with the ettringite reaction or is the result of reaction other than the formation of ettringite. Gypsum, in addition to ettringite, can be produced during sulfate attack and is capable of producing expansion.

Two particular mechanisms for expansion associated with the formation of ettringite have been widely published - the topochemical reaction mechanism [2] and the swelling mechanism [3]. According to the topochemical reaction theory of expansion, sulfate and calcium ions in the concrete pore fluid react with dissolving aluminate ions near the surface of the solid phase, and the ettringite produced by this reaction grows perpendicular to the original solid surface. Since the sulfate and calcium ions are in solution, only the volume of the aluminate phase is considered when

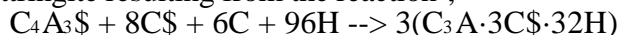
comparing volume of reactants to the volume occupied by the ettringite produced. In an open system where the concrete is permeable to water present in the environment, water may then occupy the newly formed pore space, producing an expansion.

According to the swelling theory of expansion, poorly crystalline ettringite produces expansion by adsorption of water. In a system containing sufficient concentrations of sulfate, hydroxyl, and calcium ions, small, nearly colloidal ettringite is believed to form. Water from the environment outside the concrete member is adsorbed by the poorly crystalline ettringite, generating an osmotic pressure. If the elastic modulus of the concrete is sufficiently low, a volumetric expansion of the member results.

Thus, the mechanism responsible for expansion caused by sulfate attack in concrete is uncertain. It is possible that both theories described above are valid under certain conditions. An improved understanding of behaviors occurring at the ettringite/pore solution interface is critical in developing a total appreciation for the mechanisms responsible for expansion of concrete from sulfate attack. Because interest in the reaction is focused upon the adsorption of water and the effect of ion concentration on the ettringite produced, the use of an instrument that allows the microscopic study of the reaction and the reaction product in a wet environment is integral for understanding the reaction and conditions required for expansion.

EXPERIMENT

The morphology of the ettringite resulting from the reaction*,



was examined through transmission x-ray microscopy. The $C_4A_3\$$ was made by heating a blended mixture of calculated amounts of calcium carbonate, alumina, and gypsum to 1300C in a furnace. The $C\$$ was obtained by heating gypsum to 150C. The C was obtained by decomposing calcium carbonate at 600C. A calcium sulfoaluminate mixture containing 30.0% $C_4A_3\$$, 53.5% $C\$$, and 16.5% C by weight was prepared and stored at 150C.

In addition, 0.1M $CaCl_2$ solution was substituted for water (H) in the above equation. The purpose of this substitution was to study the effect of increased concentrations of Ca^{++} on the product morphology. The images can be analyzed with respect to the theories described above to impart information concerning the expansive behavior of ettringite in some concrete systems. The reaction product of the calcium sulfoaluminate mixture in water is shown in Fig.1, and the reaction product of the calcium sulfoaluminate mixture in 0.1M $CaCl_2$ solution is shown in Fig. 2.

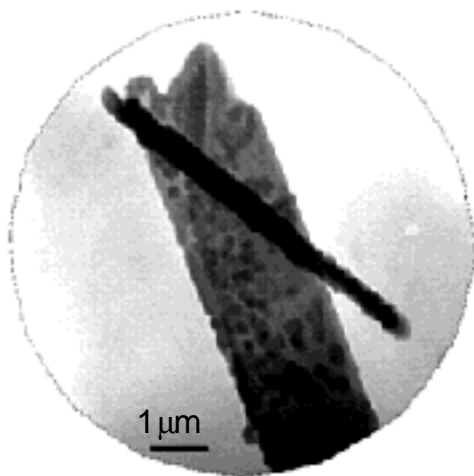


Figure 1
Calcium sulfoaluminate mixture in water.
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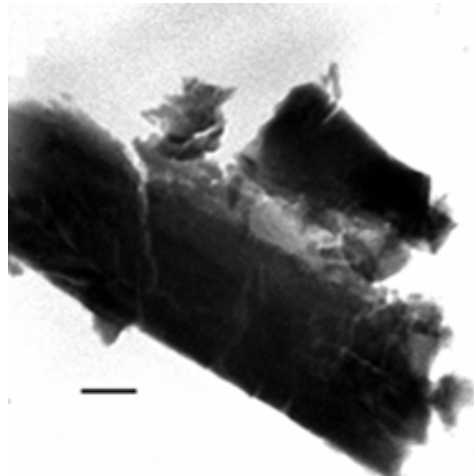


Figure 2
Calcium sulfoaluminate mixture in 0.1M
 $CaCl_2$ solution. 80131011

* In cement chemistry notation: C=CaO, A= Al_2O_3 , $\$$ = SO_3 , H= H_2O .

CONCLUSION

Variations in the morphology of the products of the calcium sulfoaluminate reaction in water and in 0.1M CaCl₂ are readily apparent. Comparison of the x-ray diffraction pattern and surface charge density of each reaction product will provide further information as to the expansive nature of these products. These investigations are currently underway.

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